Single-Crystal X-Ray Diffraction Study of Na[OCN] at 170 K and its Vibrational Spectra

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The unit cell of Na[OCN] has been determined on single crystals at 170 K to have rhombohedral symmetry with the lattice parameters a = 356.79(10) and c = 1512.3(5) pm (hexagonal setting). According to the only model for which a converging refinement could be achieved, Na[OCN] crystallizes isopointal to β-NaN$_3$ in the space group $R\bar{3}m$ (no. 166, Z = 3) with a statistically disordered [OCN]$^-$ anion. The positional coordinates and displacement parameters could not be separated for the O and N end atoms of the triatomic anion. The vibrational spectra show the frequencies typical for an [OCN]$^-$ moiety with Fermi resonance between the 2δ and the ν_{sym} vibrations for which the undisturbed frequencies were calculated.

Key words: Sodium, Cyanate, Disordered Anion, Structure Elucidation, Vibrational Spectroscopy

Introduction

Sodium cyanate, Na[OCN], is a compound which is well-employed in many syntheses, but the first structure determination done in 1938 by Bassière is to our knowledge the only one reported [1]. The compound was recognized to be isopointal to β-NaN$_3$ [2], but in the same paper an ordered structure was also postulated. A detailed analysis of similar data has been performed on K[OCN] [3] which adopts the tetragonal KN$_3$ structure [2, 4] with a head-tail-flipping disorder as the isotypic Rb and Cs cyanates most probably also do.

Because Na[OCN] is not isotypic to K[OCN], and the stated results of the previous structure determination by Bassière were considered ambiguous, we wanted to find if a disordered structure as in K[OCN] [3] or an ordered structure such as Ag[OCN] [5] is more likely. Therefore, we report here the results of a single-crystal diffraction study at 170 K. Additionally, we measured the vibrational spectra of the title compound at ambient temperatures for comparison with literature data [6].

Table 1. Summary of single-crystal X-ray structure determination data on Na[OCN].

Space group (no.); Z	$R3m$ (160); 3	$R\bar{3}m$ (166); 3
CSD number	–	420929
M_r	195.03	
Crystal color	transparent colorless	
Crystal shape	rectangular block	
Crystal size, mm^3	$0.12 \times 0.10 \times 0.08$	
Crystal system	hexagonal	
a; c, pm	356.79(10); 1512.3(5)	
V, Å^3	166.72	
F(000), e	96.0	
D_{calcd}, g cm^{-3}	1.94	
μ(MoK$_\alpha$), mm^{-1}	0.3	
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD	
Radiation; λ, pm; monochromator; T, K	MoK_α; 71.073; graphite; 173(2)	
Ranges, $2\theta_{\text{max}}$, deg; h, k, l	56.93; $-4 \rightarrow 3$, ± 4, $-12 \rightarrow 19$	
Distance detector-crystal, mm	39	
Number of frames	646	
Exposure time, s	30	
Data correction	LP	
Refls measured	316	316
unique	115	71
Unique refls with $F_o \geq 4\sigma(F_o)$	112	68
R_{int}	0.0144	0.0147
Refined parameters	13	8
$R1^a/wR2^b$	0.0233/0.0652	0.0215/0.0639
GooF^c (all refls)	1.195	1.251
Factors x/y (weighting scheme)^b	0.0301/0.24	0.0355/0.1152
x(Flack) [11]	1.4(23)	–
Max. shift / esd, last refinement cycle	< -4.54	< 0.0005
$\Delta\rho_{\text{fin}}$ (max, min), e Å^{-3}	0.16 (1 pm to N), −0.20 (85 pm to Na)	0.16 (79 pm to O), −0.18 (72 pm to Na)

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF = $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Experimental Section

Synthesis

0.4 g (6.15 mmol) of Na[OCN] (Aldrich, powder, ACS grade) was filled into a silica ampoule, evacuated and sealed.

Table 2. Atomic coordinates, isotropic[a] and anisotropic[b] displacement parameters (pm^2) of Na[OCN].

Atom	Wyckoff site	x	y	z	$U_{11} = U_{22}$	U_{33}	U_{12}	U_{eq}[a]
Refined in $R3m$ (no. 160)								
Na	3a	0	0	0.0057(3)	170(5)	139(10)	85(3)	159(5)
N	3a	0	0	0.5852(3)	171(36)	175(52)	85(18)	172(26)
C	3a	0	0	0.5041(10)	123(9)	228(19)	61(4)	158(7)
O	3a	0	0	0.4253(2)	264(40)	262(48)	132(20)	263(30)
Refined in $R\bar{3}m$ (no. 166)								
Na	3a	0	0	0	166(5)	148(6)	83(2)	160(4)
C	3b	0	0	1/2	118(8)	213(13)	59(4)	150(6)
O / N	6c	0	0	0.4199(1)	214(6)	203(8)	107(3)	211(5)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors; [b] the anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

The ampoule was placed into a tube furnace and heated to 800 K within 13 h. After 3 h at this temperature the furnace was switched off and allowed to cool to r. t. The product contained a transparent, colorless, solidified block consisting of single-crystalline Na[OCN] which could be cut into single-crystal fragments suitable for X-ray diffraction studies. In the form of single crystals, the compound withstands air and moisture over several days without any noticeable change of the diffraction pattern or in appearance visible to the naked eye.

Table 3. Selected atomic distances (pm) and angles (deg) in Na[OCN].

Refined in space group $R3m$ (no. 160) (ordered model)			Refined in space group $R\bar{3}m$ (no. 166) (disordered model)		
Atoms		Distance	Atoms		Distance
Na–O	3×	243.8(3)	Na–N / O	6×	244.1(1)
–N	3×	244.5(4)			
C–O	1×	119.2(17)	C–O / N	2×	121.1(2)
–N	1×	122.7(16)			
∡(N–C–O)	1×	180	∡(N–C–O)	1×	180

Crystallographic studies

Samples of the compound were immerged into polybutene oil (Aldrich, $M_n \sim 320$, isobutylene $> 90\,\%$). A suitable single crystal of Na[OCN] was selected under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. This ensemble was cooled with a cold stream of nitrogen in a matter of seconds to T = 170(2) K. This temperature was kept steady during the whole intensity measurement. At this temperature, the polybutene oil froze. Therefore, not only was the crystal kept stationary and protected from oxygen and moisture in the air, but also the thermal motion of the [OCN]$^-$ anion was less than would be the case at r. t. We also assumed that it would be easier at lower temperature to detect a superstructure or any order in the orientation of this unsymmetrical anion. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the respective lattice parameters were obtained by using APEX2 [7]. No superstructure reflections were detected by tripling the exposure time of the orientation frames. The program SAINT [8] was used to integrate the data. No absorption correction was applied. The program XPREP [9] found the space groups $R3m$ (no. 160) and $R\bar{3}m$ (no. 166) to fulfill the reflection conditions best. As starting models, the crystal structure reported by Bassière [1] – transformed to a hexagonal setting – was used for the space group $R3m$, while for the space group $R\bar{3}m$ the positional parameters known for β-NaN$_3$ [2] were used as starting model. In the latter case, the end atoms share the same crystallographic position. To achieve this, the O and N atoms were constrained not only to be refined on the same crystallographic position, but also to have the same displacement parameters. The refinements of the structures were performed by full-matrix least-squares techniques with the use of SHELXL-97 [10]. Doing further refinement cycles, the refinement converged for the second model with the disordered β-NaN$_3$ structure [2] and resulted in a stable model while the Bassière model did not converge. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2, Table 3 displays selected bond lengths and angles.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html), on quoting the deposition number CSD-420929.

Vibrational spectra

Raman investigations (microscope laser Raman spectrometer: Jobin Yvon, 1 mW, excitation line at λ = 632.817 nm (HeNe laser), grating: 1800 lines/mm, 100× magnification, samples in glass capillaries, 10×90 s accumulation time) were performed on the same specimen used for single-

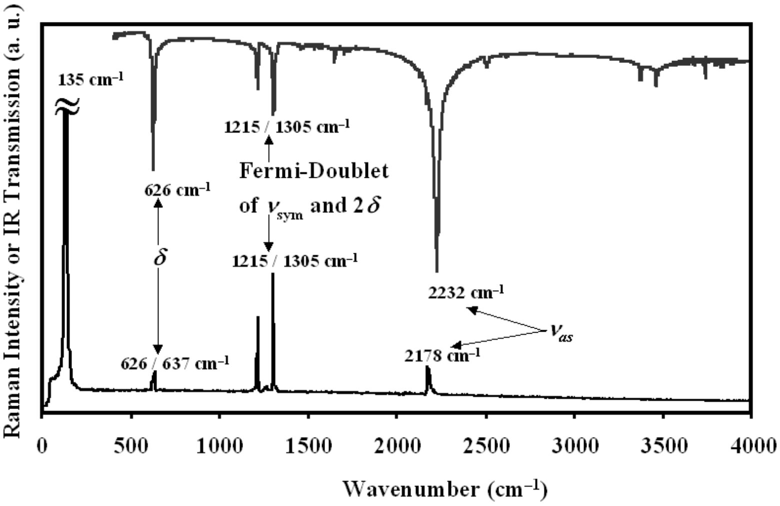

Fig. 1. Vibrational spectra of Na[OCN].

crystal measurements. IR investigations were carried out with a Bruker AFS 66 FT-IR spectrometer. About 1 – 5 mg Na[OCN] was ground in an agate mortar with 450 – 500 mg of thoroughly dried KBr and pressed into a pellet.

The vibrational spectra for solid Na[OCN] were recorded in the region from 0 to 4000 cm^{-1} (Raman spectrum) and from 400 to 4000 cm^{-1} (IR spectrum). The results of the optical measurements are displayed in Fig. 1.

Table 4. Fundamental frequencies (cm^{-1}) for sodium and potassium azides and cyanates. Frequencies obtained by Raman measurements are printed bold, IR results are given in italics, and calculated values are given in parentheses.

	δ	2δ	ν_{sym}	ν_{as}	Ref.
β-NaN_3	*637*	**1269**	**1360**	*2037*	[12]
KN_3	*649*	**1271**	**1342**	*2035*	[12]
Na[OCN]	***626***	(1268)	(1251)	**2178**	this work
	637	***1304***	***1215***	*2232*	
Na[OCN]	*620*	*1305*	*1216*	*2220*	[6]
K[OCN]	**630**	(1262)	(1245)	**2181**	[13]
	638	**1300**	**1207**		

Results and Discussion

Vibrational spectra

As expected, the spectra differ from those reported for β-NaN_3 [12] in some respect despite their structural similarity. N_3^- anions have $D_{\infty\mathrm{h}}$ symmetry where the antisymmetric stretching vibration ν_{as} and bending mode δ are only IR active while the symmetric stretching vibration ν_{sym} is exclusively Raman active, but for the $[OCN]^-$ anion in Na[OCN] with lower $C_{\infty\mathrm{v}}$ symmetry, all fundamental modes are both Raman and IR active (Fig. 1 and Table 4). The antisymmetric stretching vibration ν_{asym} appears at 2178 cm^{-1} in the Raman spectrum while this mode shows in the IR spectrum at 2232 cm^{-1}. The bending mode δ is degenerate in the IR spectrum at 626 cm^{-1} while in the Raman spectrum this mode is split and observed at 626 and 638 cm^{-1}. As observed for K[OCN] [13], the symmetric stretching mode ν_{sym} couples with the first harmonic overtone of the bending mode 2δ and shows Fermi resonance [13, 14] which occurs both in the IR and the Raman spectrum. By this effect, the overtone usually grows in intensity while the fundamental vibration loses intensity. The two peaks 'repell' each other to lower and to higher frequencies, respectively. The shift is in both spectra nearly the same, and the Fermi-doublet shows at 1215 and 1305 cm^{-1}. The relative intensities and the seperation of the maxima depend on how closely the undisturbed frequencies fall, and these can be calculated with the following expression [13, 14]:

$$\nu_{\mathrm{corr.}} = \frac{\nu_{\mathrm{a}}+\nu_{\mathrm{b}}}{2} \pm \frac{\nu_{\mathrm{a}}-\nu_{\mathrm{b}}}{2} \cdot \frac{I_{\mathrm{a}}-I_{\mathrm{b}}}{I_{\mathrm{a}}+I_{\mathrm{b}}}$$

The measured and corrected frequencies are displayed in Table 4. The corrected modes were assigned following the general rules mentioned above and in analogy to the spectra of K[OCN] [13, 14].

Crystal structure

The crystal structure of Na[OCN] is isopointal to that of β-NaN_3 [2]. In both compounds, the Na^+ cations form close-packed layers in a cubic stacking

Table 5. Atomic distances and angles in different compounds of the type M^{+I}[OCN][a].

Compound	d(N–C) / d(C–O)	∡(N–C–O)	Ref.
Na[OCN] (#166)	121.1 / 121.1	180	This work
Na[OCN] (#160)	122.7 / 119.2	180	This work
Na[OCN] (Bassière)	120.8 / 113.3	180	[1]
K[OCN]	120.0 / 120.0	180	[3]
Rb[OCN]	117.6 / 117.6	180	[6]
Cs[OCN]	123.4 / 123.4	180	[6]
Tl[OCN]	116.3 / 116.3	180	[6]
Ag[OCN]	117.1 / 118.3	171.7	[5]
NH_4[OCN]	119.2 / 117.4	180	[16]

[a] The corresponding azides are all symmetrical having an azide bond angle of 180° and atomic distances between 116.0 (TlN_3) [12] and 118.8 (AgN_3) [17].

$\cdots$ABCABC$\cdots$. The Na^+ layers are held together by the respective triatomic anions, which are embedded in the octahedral voids. Alternatively, the structure can be described as a rhombohedrally, along [111] distorted rocksalt structure in which the anions are orientated parallel to [111]. Because the $[N{=}N{=}N]^-$ anion is symmetrical, the only remaining question for the $[O{=}C{=}N]^-$ anion is if there is a superstructure, a frustration problem, a lowering of the symmetry connected with layerwise ordered anions, or if there are statistically disordered anions present with just the same 'average' symmetry as in β-NaN_3 [2]. As mentioned above, no superstructure reflections were detected with extended exposure time indicating that there is no layerwise antiparallel ordering of the $[OCN]^-$ anion. An antiparallel orientation of the anion within each layer would lead to a frustration problem as observed, *e. g.*, for $Na_{22}Ba_{14}CaN_6$ [15]. Since diffuse scattering around the Bragg reflections typical for a frustrated order can only be observed on Laue photographs taken with a precession camera and long exposure times, our studies can not exclude a frustration problem. The X-ray scattering powers of O, C and N are quite similar, therefore, no definite proof can be given for either the structural model suggested by Bassière or the statistically disordered β-NaN_3 model. The positional and displacement parameters of Na and C agree in both models within the respective estimated standard deviations. Nevertheless, the refinement of both models under discussion only converged for the β-NaN_3 model [2] with a disorderd anion. That model also has slightly lower R values and fewer refined parameters. Also the meaningless Flack parameter [11] of 1.4(23) (twin refinement did not improve the result) and the large estimated standard deviations for the atomic distances (Table 3) speak for the disordered model refined in $R\bar{3}m$. The atomic distances obtained for the different models are somewhat inconclusive (Table 5) because the disordered β-NaN_3 model basically just shows – as expected – the average of the distances and displacement parameters obtained by the Bassière model. Reliable data for pseudobinary monovalent or divalent (iso)cyanates for comparison are not numerous and usually come with large standard deviations, since they were not obtained with state-of-the-art methods.

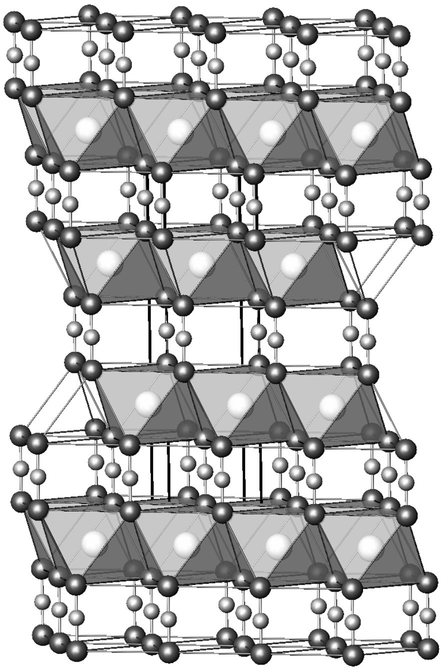

Fig. 2. Perspective view on the unit cell of Na[OCN] perpendicular to the crystallographic c axis. The coordination octahedra of Na^+ cations (displayed as white spheres) are drawn as grey, open octahedra, C and O/N are displayed as light grey or black spheres.

Conclusion

The vibrational spectra of Na[OCN] are reported to correct some previously reported data, and the fundamental frequencies perturbed by Fermi resonance are corrected. The X-ray single-crystal diffraction study of Na[OCN] gives a picture of the 'frozen' r. t. crystal structure of this compound. Next to other indications, the only converging refinement of the collected X-ray intensity data was achieved for Na[OCN] crystallizing in the space group $R\bar{3}m$ (no. 166, Z = 3), suggesting that the title compound is isopointal to β-NaN_3 with a disordered $[OCN]^-$ anion (Fig. 2).

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